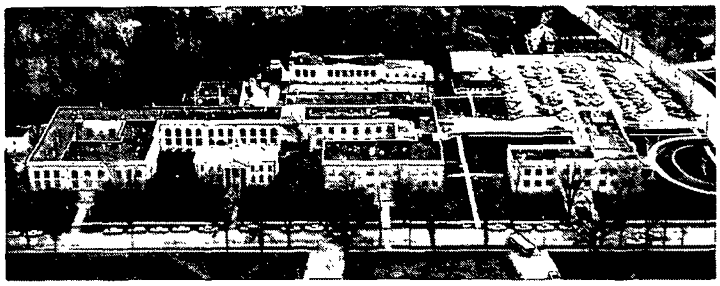

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SIGNIFICANCE OF METHANOL RECOVERY TO KRAFT MILL TOTAL ENERGY BUDGET

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Abstract

The paper industry is the fourth largest industrial consumer of energy in the United States. However, because of its ability to generate energy from its own waste products, it is in a unique position. More than one-third of the industry's energy requirements are now self-generated. As the energy situation continues to worsen, additional energy sources from waste residues will be sought.

Methanol contained in wastewater streams generated during the kraft pulping process has traditionally been sewered because it cannot be economically recovered. As the cost of energy increases, more mills will examine the feasibility of recovering methanol. This paper reviews the energy value of the methanol produced during kraft pulping and relates it to the average specific energy consumption of the paper industry.

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Introduction

The manufacture of pulp and paper is an energy intensive process. Major requirements for energy are in the pulping of wood at relatively high temperatures and pressures, in the subsequent recovery of pulping chemicals, and in the drying of the final product. Taken as a whole, the paper industry is the fourth largest industrial consumer of energy in the United States [1].

Fortunately, because of the nature of its operations, the paper industry is able to generate much of its own energy requirements from wood residues. The American Paper Institute routinely monitors energy usage within the industry. In a recent study [2] they compare energy requirements for the first six months of 1972 to the first six months of 1976. Although there was more than an 11% increase in total production during the study period, there was about a 4% decline in total energy consumption to approximately 2.210×10^{10} J. Moreover, the amount of purchased energy decreased from 1.343×10^{18} J in 1972 to about 1.217×10^{18} J in 1976. As the energy situation worsens, the response of the paper industry will undoubtedly be toward increased generation of energy from wood residues.

The objective of this communication is to review the recovery of methanol from kraft pulp mills as a potential energy resource.

Methanol Generation and Sources

Methanol is produced during the kraft pulping process by the demethylation of methoxyl groups ($-OCH_3$) found mainly on the lignin polymer. The reaction from which methanol is believed to be formed is:

$$R\text{-}OCH_3 + NaOH \rightarrow R\text{-}ONa + CH_3OH$$

The reaction has tentatively been identified as a bimolecular nucleophilic substitution (S_N2) [3,4]. The rate expression for the generation of methanol may then be represented as:

$$r = k\ [R\text{-}OCH_3][OH^-]$$

The rate constant, k, has not been determined. Although hardwoods contain significantly more methoxyl groups than softwoods, less methanol is usually formed during kraft pulping of hardwoods than softwoods. This has been attributed to the shorter pulping time, the lower temperature, and the lower pH needed for kraft hardwood pulping [5].

The nature of the kraft pulping process is such that methanol can be recovered from three condensate streams. Periodically during the pulping cycle, gases are vented to maintain a constant pressure in the digester and to purge unwanted gaseous components, mainly air. These digester relief gases, a significant source of odor in the kraft mill, are collected, condensed, and sewered. At the end of the pulping cycle, the digester contents are discharged to a blow pit by relieving the pressure from about 1.25 mn/m^2 to a pressure slightly above atmospheric. During this process, considerable steam and volatile components are flashed off. The gases from this process, termed blow gases, are also collected, condensed and sewered. The last major source of methanol comes from the condensate of the multiple effect evaporators used to recover chemicals from the spent pulping liquor. These three condensate streams contain the bulk of the methanol lost from the pulp mill. They are typically sent to the wastewater treatment plant via a common sewer. A simplified schematic of a kraft pulp mill is given in Fig. 1.

Presented in Table 1 are typical quantities of methanol from the various condensate streams. Table 2 shows the relationship of the total mill biochemical oxygen demand (BOD_5) to that from the blow gas condensate alone.

About 100 liters of digester relief condensate, 1000 liters of blow gas condensate, and 6500 liters of evaporator condensate are generated for each metric ton of pulp production.

The data in Table 1 indicate a significant quantity of methanol could be recovered. At present, nearly all mills sewer these condensate streams which eventually exert an oxygen demand at the wastewater treatment plant.

Removal of Methanol

The feasibility of air stripping combined condensate has been demonstrated during pilot-plant tests. A typical air stripping system is shown in Fig. 2. To carry out the stripping process, it is necessary to contact the condensate with large volumes of air in order for mass transfer of methanol from the aqueous to the gas phase to occur. The driving force for the mass transfer of any component is the difference in the equilibrium vapor pressure at the gas/liquid interface and the partial pressure in the air stream. The gas/liquid equilibrium vapor pressure increases as the component concentration in the aqueous phase increases and also as the liquid phase temperature increases. The partial pressure of any component in the air stream will depend primarily on the throughput of air into the stripper. It is not always beneficial, however, to supply as much air as possible to the stripper because the air stream will cool the liquid to be stripped by evaporative cooling. It is reported that in one situation condensate entered the stripper at about 77°C and left at 54°C [6].

Air stripping is typically used where it is desirable to strip both methanol and odorous reduced sulfur compounds, e.g., H_2S, CH_3SH, $(CH_3)_2S$, and $(CH_3)_2S_2$, from the condensate. In these cases, the design will be for about 90% of the reduced sulfur compounds; under these circumstances, only about 10-20% of the BOD (largely methanol) is removed concurrently [7]. The stripper gases are finally sent to an incinerator for final destruction. No attempt is made to recover the methanol.

Pilot-plant tests [8] revealed that at an air-condensate volumetric ratio of 10, about 45% of the malodorous reduced sulfur compounds were removed while only about 15% of the methanol was removed. When the volumetric ratio was increased to 20, there was essentially complete removal of reduced sulfur compounds but the percentage of methanol stripped fell to 8. No explanation was given for this decrease. Another benefit of air stripping demonstrated in this report was the decrease in toxicity of the stripped condensate toward common bioassay organisms. It is also important to size the air system to ensure that the stripped gases are below their lower explosive limit. Based on these pilot plant data, a full scale system was installed at a 500 metric ton/day mill. Full-scale results compare favorably with the pilot plant.

Steam stripping is more effective in removing methanol because the process takes place at the condensate stream boiling point. Because the equilibrium vapor pressure and, thus, the rate of methanol mass transfer, are greater as the temperature increases, more methanol can be removed in steam stripping as compared to air stripping. Figure 3 shows a typical steam stripping schematic. Additional equipment is required to condense the methanol vapor and to recover the turpentine that is also stripped.

Steam stripping has been reported on both pilot plant and mill scale. The SEKOR (Stripping Effluents for Kraft Odor Reduction) Project demonstrated on a pilot scale that effective removal of alcohols would accompany stripping of reduced sulfur compounds [9,10]. A gravimetric ratio of 10 between condensate and steam was required to strip about 70% of the methanol and essentially all of the reduced sulfur compounds in one pilot-plant study [8].

Reports from mill experiences emphasize the economics of the process and how it may be integrated with the total mill energy budget. One mill [11] found that the use of vapor compression evaporation greatly increased total system economics. Another mill [12] combined vapor compression evaporation and a distillation tower to remove methanol. The stripped condensate is renovated for pulping liquor makeup and pulp washing. By stripping methanol and other contaminants from condensates, one mill was able to increase production without having to increase the size of the treatment plant [13]. Methanol was recovered as a 15% aqueous solution. No auxiliary fuel was required to burn this in the lime kiln.

Energy Analysis

The average specific energy consumption is about 2.465×10^{10} J/metric ton of pulp produced in the United States paper industry [14]. If methanol is removed from the pulp mill wastewater, two energy credits can be taken. First, the recovered methanol may be used as a fuel and, second, the oxygen demand in the waste treatment plant, due to methanol, is removed. From the data in Table 1, about 5 kg of methanol per metric ton of pulp produced can be expected. The heating value of methanol is 6.264×10^6 J/kilograms [15]. Thus, if all the methanol could be recovered as fuel, about 3.13×10^9 J of energy would be gained. In addition to this, about 7.2×10^6 J of energy would be saved in the wastewater treatment plant by not having to transfer oxygen to the secondary treatment system to meet the oxygen demand of the methanol. This estimate was made by assuming that 1 kg of methanol would exert 0.7 kg of BOD_5, 1.1 kg O_2 must be supplied per kilogram of methanol treated (at a mean cell residence time of 8 days in the secondary treatment plant), and oxygen could be transferred at a rate of 2.1 kg O_2/kw-hr. Thus, it is estimated that approximately 13% ($3.137 \times 10^9 \div 2.465 \times 10^{10} \times 100\%$) of the average specific energy consumption can be supplied from the recovered methanol.

Obviously, if it were cost effective to recover methanol from condensate streams, all kraft mills would practice it. However, nearly all kraft mills were built before the advent of the energy crisis. Thus, most mills would have to bear the cost of expensive retrofitting of recovery equipment and repiping of sewers. Of the three basic processes used to recover methanol, air stripping, steam stripping, and distillation, no one of them can be applied to all mills [16]. Each mill will have to perform its own feasibility study before cost effectiveness for any recovery process can be determined. It would appear, however, that any scheme will require substantial capital expenditures and also will incur significant operating charges to generate the energy required to strip or distill the methanol. A significant portion of the energy recovered from methanol will in turn have to be used in the methanol recovery process. The impact of any methanol recovery proposal on the total energy budget will have to be determined for each specific mill.

Summary

Significant quantities of methanol are produced as a by-product of the kraft pulping process. Because most kraft mills were built before the advent of the current energy situation, methanol recovery is not normally practiced. However, several process flowsheets have been developed to recover the methanol before it becomes a load on the waste treatment plant.

Current mill experience shows that the cost of methanol recovery can be offset by its recovered fuel value. However, little, if any, net energy is generated. The principal justifications for methanol removal seem to be a reduction of load to the waste treatment plant and substantial removal of odorous and toxic compounds concurrent with methanol stripping.

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TABLE 1

Methanol content of condensate streams in a kraft mill with various wood species being pulped (after 5)

Condensate stream	Methanol content (kilogram/metric ton air-dried pulp) Pine	Birch	Alder: Douglas-fir (∿4:1)	Cedar: Douglas-fir (∿4:1)
Digester relief	0.70–0.85	0.80	1.00	0.35
Blow gas	0.90–0.95	0.55	2.05	1.85
Evaporator	4.65–6.15	4.00	2.60	2.60
Total	5.75–7.95	5.35	5.65	4.80

TABLE 2

BOD discharge and flow rate from one unbleached kraft mill[a]

Source	Flow		BOD_5	
	m^3/min	% of Total	kg/day	% of Total
Total mill	63.0	100.0	6820	100
Pulp mill	5.3	8.0	6045	88
Blow gas condensate	0.3	0.5	4320	63
Methanol contribution to total blow gas condensate	--	--	1700[b]	25

[a]Nominal capacity of 900 metric ton/day.

[b]Assumes 0.7 kg BOD_5/kg methanol.

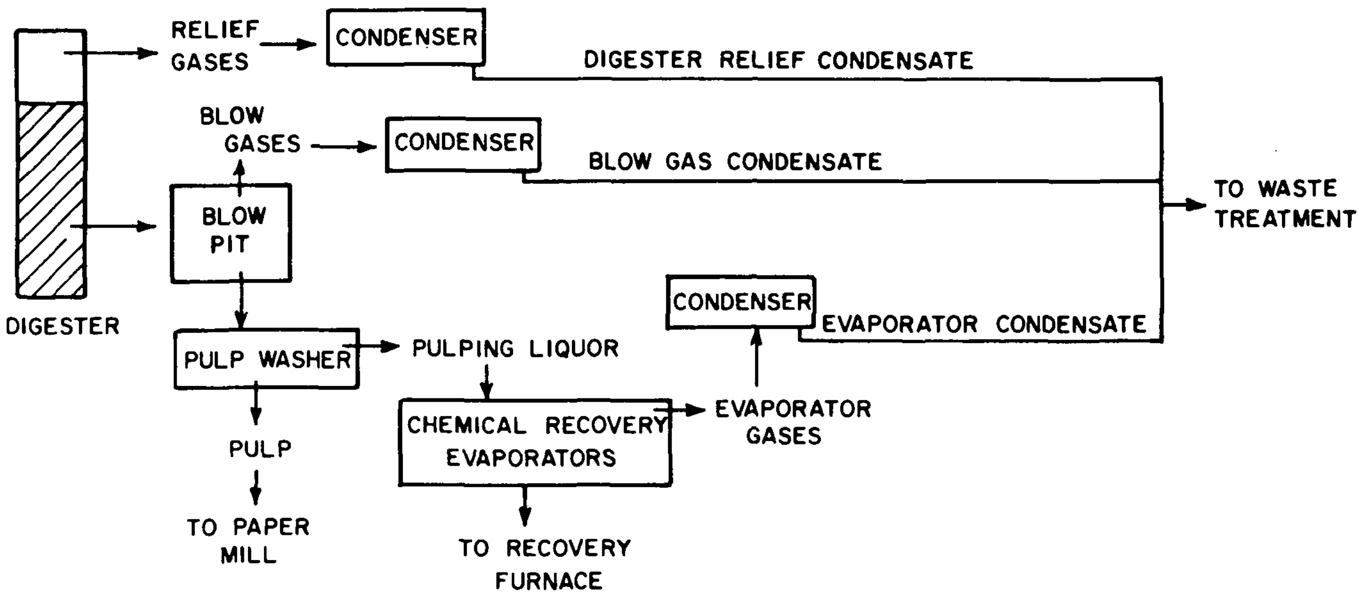

Fig. 1. Condensate streams in the kraft pulping process.

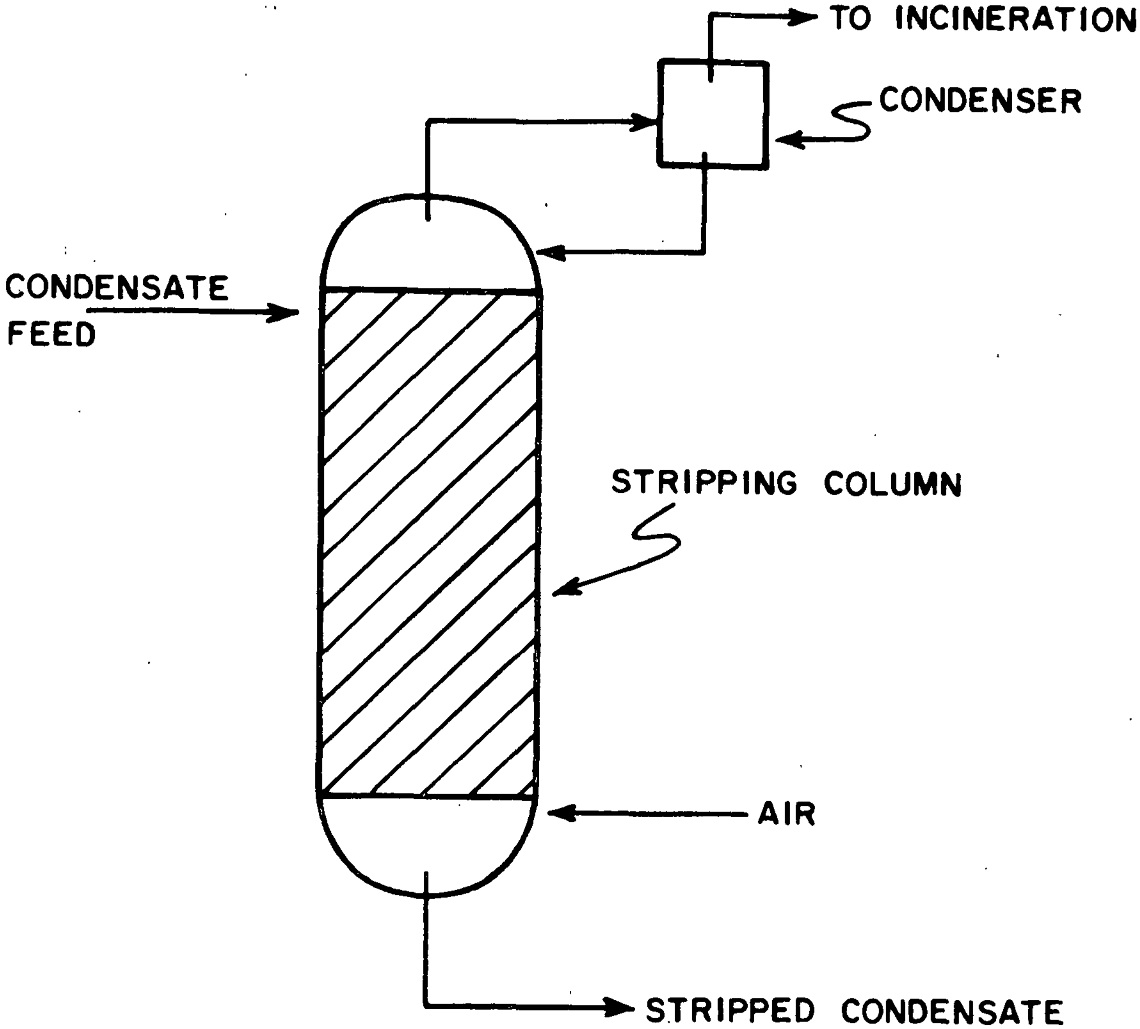

Fig. 2. Air stripping schematic.

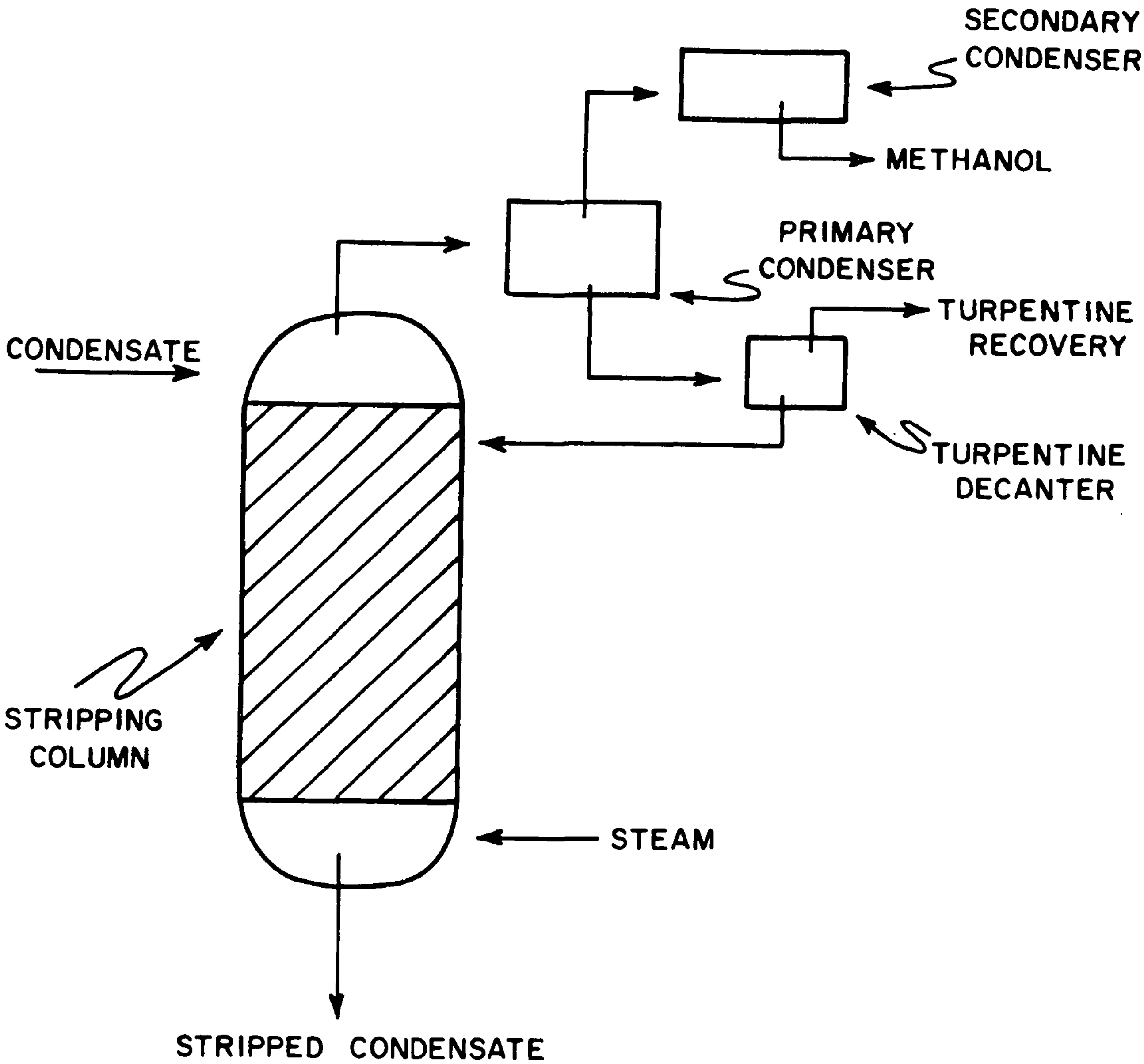

Fig. 3. Steam stripper schematic.